

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11) Publication number:

0 088 527  
A2

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 83300754.5

(51) Int. Cl.: A 61 K 6/08, C 08 L 43/02,  
C 07 F 9/09

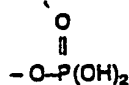
(22) Date of filing: 15.02.83

(30) Priority: 16.02.82 GB 8204511

(71) Applicant: Dentsply Limited, Hamm Moor Lane  
Addlestone, Weybridge Surrey (GB)(43) Date of publication of application: 14.09.83  
Bulletin 83/37(72) Inventor: Billington, Richard William, 96 Cranbrook Road,  
Chiswick London W4 (GB)  
Inventor: Blackwell, Gordon Brian, 10 Hampshire Road,  
Camberley Surrey (GB)  
Inventor: Prodger, Terence Ernest, 9 Downsview Road,  
Horsham Sussex (GB)(84) Designated Contracting States: CH DE FR GB IT LI NL  
SE(74) Representative: Lamb, John Baxter et al, Marks &  
Clerk 57/60 Lincoln's Inn Fields, London WC2A 3LS (GB)

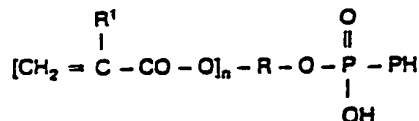
(54) Adhesion promoters.

(57) An adhesion promoter for promoting the adhesion of a reduced polymerizable composition to a substrate, particularly for promoting the adhesion of radical polymerizable dental composition to tooth material, comprises a polyethylenically unsaturated monophosphate or salt thereof, the unsaturated monophosphate containing a monophosphate radical of the formula:



and at least three ethylenically unsaturated groups per molecule.

Preferred polyethylenically unsaturated phosphates are monophosphates of polyhydric alcohols containing at least four hydroxyl groups in which at least three hydroxyl groups are esterified with an ethylenically unsaturated carboxylic acid. Especially preferred unsaturated phosphates, which are provided as a feature of the invention, are those of the formula:



in which R is an aliphatic radical (which may be interrupted by one or more oxygen atoms), or a cycloaliphatic or aryl radical having a valency of R + 1 and containing from 4 to 16 carbon atoms; R<sup>1</sup> is a hydrogen or halogen atom or a cyano or C<sub>1</sub>-C<sub>3</sub> alkyl group; and n is an integer of at least 3.

The polyethylenically unsaturated monophosphate may be first applied to the substrate, e.g. as a volatile organic solvent solution thereof, and the reduced polymerizable material then applied to the substrate and polymerized thereon. Alternatively, the polyethylenically unsaturated monophosphate may form part of a radical polymerizable dental filling material applied to tooth material.

ADHESION PROMOTERS

This invention is concerned with improvements in and relating to adhesion promoters, especially for use in promoting the adhesion of addition polymerizable dental materials to natural teeth.

5           Addition polymerizable dental materials, such as filling materials, cements and the like, generally comprise a mixture of a finely divided inert filler with one or more ethylenically unsaturated materials capable of in situ polymerization in a dental cavity to form a hard  
10           filling material. A wide variety of fillers may be employed and examples thereof include finely divided glasses, ceramics and inorganic oxides containing e.g. silicon and aluminium. The filler will generally have been subjected to an appropriate surface treatment such as silanation or with a titanate. The finely divided inert filler may form less than 50% by weight of the composite material, but commonly  
15           forms from 50 to 85% by weight thereof and especially from 60 to 80% by weight thereof. The inert filler suitably has an average particle size of from 1 to 100, preferably from 1 to 60 microns. Such a filler may be replaced by, or used in admixture with a superfine  
20           filler, e.g. having a particle size of from 10 to 400 millimicrons as disclosed in British Patent Specification No. 1,488,403, in which case the filling material may contain lower amount, e.g. 30-50% by weight, of filler.

          Other addition polymerizable dental materials comprise a mixture of an organic filler, e.g. a polymer or copolymer of methyl methacrylate,  
25           together with an ethylenically unsaturated material, typically methyl methacrylate.

The ethylenically unsaturated component or binder of the composite material generally comprises one or more esters of ethylenically unsaturated carboxylic acids, especially of acrylic or methacrylic acid. Thus the ethylenically unsaturated binder component may comprise simple esters of unsaturated carboxylic acids with monohydric aliphatic alcohols, for example methyl (meth)acrylate, ethyl (meth)acrylate and 2-ethylhexyl (meth)acrylate.

(In this specification the term "(meth)acrylate" is intended to refer to an acrylic or methacrylic acid ester of a hydroxyl group-containing compound).

Further, the unsaturated component may comprise unsaturated carboxylic esters of polyhydric alcohol, especially polyhydric alcohols containing one or more phenyl groups, such as the adduct of bisphenol A and glycidyl methacrylate, Bisphenol A (meth)acrylate and/or reaction products of 2-hydroxyethyl (meth)acrylate with isophthalic, terephthalic or phthalic acid chloride. Another class of ethylenically unsaturated binder comprises the adducts of 2,2 propane-bis 3-(4-phenoxy)-1,2-dihydroxy propane-1-methacrylate and an isocyanate or diisocyanate as described in U.S. Patent No.3,629,187. Yet another class of ethylenically unsaturated material which may be present in the ethylenically unsaturated binder component comprises the reaction products of monoesters of dihydric alcohols (e.g. ethylene glycol mono(meth)acrylate) with polyisocyanates especially aliphatic diisocyanates such as 2,2,4-trimethyl-hexamethylene diisocyanate or hexamethylene diisocyanate. In practice a mixture of two or more ethylenically unsaturated materials may be, and commonly is, employed.

The unsaturated component may also comprise an unsaturated fluorine-containing material, as disclosed for example in United States Patent No. 4292029, which additionally serves to reduce penetration of fluids between tooth surfaces and restorative material.

5           The composite materials should also contain, when filled into a tooth cavity, a polymerisation initiator for effecting polymerisation of the ethylenically unsaturated binder component. Such initiator should, of course, be capable of initiating polymerisation at comparatively low temperatures, i.e. mouth temperatures, and examples of suitable  
10           initiators include organic peroxides, such as benzoyl peroxide or tert.butyl peroctanoate, desirably together with an activator e.g. a tertiary amine activator such as dimethyl paratoluidine, or ascorbic or sulphinic acid or a salt thereof. In an alternative procedure the composite filling material may contain an initiator sensitive  
15           to visible or ultraviolet light which, on exposure to such light, initiates polymerisation of the ethylenically unsaturated binder component. Examples of such initiators include chlorobenzophenone and benzoin methyl ether (for U.V. light) and camphorquinone (for visible light). In some cases an accelerator, such as a secondary  
20           or tertiary amine, may also be employed in order to accelerate the reaction.

          It is most desirable, when filling a tooth cavity with a composite filling material, to ensure good adhesion between the enamel on the tooth surrounding the cavity and the set (polymerised) composite  
25           material since there is thereby obtained a good seal between the

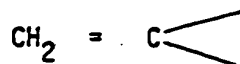
set composite material and the enamel of the tooth which prevents, or at least markedly inhibits, ingress of mouth fluids into the filled cavity and so prevents further decay or loss of the filling. In order to achieve good adhesion between the filling material and the tooth enamel it has been recommended to subject the enamel to an acid etch, for example with 30 - 50% aqueous phosphoric acid or 55% aqueous orthophosphoric acid buffered with zinc oxide. This procedure, however, is time-consuming and, naturally, involves the loss or removal of some tooth enamel.

It has now been found, in accordance with the present invention, that the adhesion of a composite material, as described above, to tooth enamel may be markedly improved by firstly applying to the tooth enamel a compound comprising a monophosphate radical (that is a group of the formula -  $\overset{\text{O}}{\underset{\text{O}}{\text{P}}} - (\text{OH})_2$ ) and at least three ethylenically unsaturated groups. The composite filling material is then introduced into the cavity and cured therein, with concomitant polymerisation of the poly unsaturated phosphate. As a result it is found that the adhesion of the set composite filling material to the enamel is markedly improved, as compared with a comparable process wherein no poly unsaturated phosphate is employed, and there may be achieved degrees of adhesion comparable to those obtained with prior acid etching of the enamel.

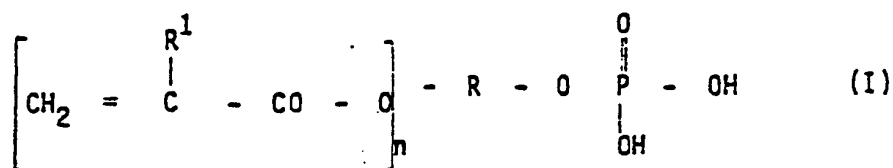
According to one embodiment of the invention, therefore, there is provided an adhesion promoting composition suitable for improving the adhesion of a composite dental filling material to natural teeth comprising a solution, in a volatile organic solvent therefor, of an ethylenically unsaturated monophosphate or salt thereof. the ethylenically unsaturated monophosphate containing a monophosphate radical and at least three ethylenically unsaturated groups per molecule.

Suitable volatile organic solvents for use in the compositions of the invention include lower aliphatic alcohols, especially ethanol, and the concentration of the ethylenically unsaturated monophosphate in the solution is suitably from 0.5 to 10%, preferably from 0.5 to 2.5%, especially about 1%, by weight.

The ethylenically unsaturated groups in the ethylenically unsaturated monophosphate are preferably terminal or vinyl groups of the formula:



A particularly preferred class of unsaturated phosphates for use in accordance with the invention are monophosphates (orthophosphoric acid monoesters) of polyhydric alcohols containing at least four hydroxyl groups in which at least three hydroxyl groups are esterified with an ethylenically unsaturated carboxylic acid, especially acrylic or methacrylic acid. Thus, one preferred class of polyethylenically unsaturated monophosphate for use in accordance with the invention may be represented by the formula:



in which:

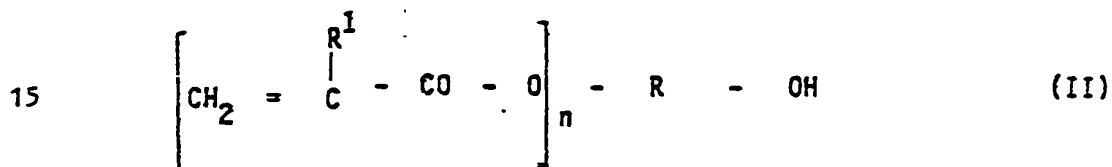
R is an aliphatic radical, which may be interrupted by one or more oxygen atoms, or a cycloaliphatic or aryl radical having a valency of  $n + 1$  and containing from 4 to 16 carbon atoms;

$R^1$  is a hydrogen or halogen atom or a  $C_1-C_3$  alkyl or -CN group; and

$n$  is an integer of at least 3, preferably from 3 to 6.

Particular examples of such compounds include pentaerythritol  
 5 tri(meth)acrylate monophosphate and dipentaerythritol penta(meth)-  
 acrylate monophosphate. The compounds of formula (I) are in themselves  
 new compounds and are provided as a further feature of the invention.

The compounds of formula (I), and other ethylenically unsaturated  
 monophosphates, may also be used in the form of their salts, for  
 10 example alkali metal (e.g. sodium or potassium) or ammonium salts.  
 Polyethylenically unsaturated monophosphates of formula (I) may be  
 prepared by phosphorylating, (e.g. by reaction with phosphorous oxy-  
 chloride or phosphorous pentoxide) a corresponding monohydroxy compound  
 of the formula:



in which R,  $R^1$  and n have the meanings defined above.

In some cases adhesion may be enhanced by the use of an  
 intermediate bonding resin, e.g. a polymerisable ethylenically unsatu-  
 rated material containing little or no filler. In this case, the  
 20 solution of polyunsaturated phosphate is first applied to the tooth  
 followed by a layer of intermediate bonding resin and finally the

filling material is introduced. The intermediate bonding resin may be used before or together with the curing of the filling material.

Further, the adhesion promoters of the invention may be used to improve the adhesion of fissure sealants which are material of similar composition to the intermediate bonding resins noted above.

As noted above, the polyunsaturated phosphates may be employed to improve adhesion between a composite dental filling material and tooth enamel by first applying a composition containing the polyunsaturated phosphate to the tooth enamel and subsequently filling the cavity in the tooth with the filling material. Alternatively, the polyunsaturated phosphate may be incorporated in the filling composition itself and, accordingly, another embodiment of the invention provides a composite dental filling material comprising (i) an inert finely divided filler; (ii) an ethylenically unsaturated binder material; (iii) an initiator for the ethylenically unsaturated binder; and (iv) a poly unsaturated phosphate as defined above, i.e. containing at least three ethylenically unsaturated groups per molecule. In such compositions the proportions and contents of the filler, binder and initiator will be generally conventional and the poly unsaturated phosphate is suitably present in an amount of 1 to 20, preferably from 2 to 5% by weight, based on the total weight of the composite filling. It may be noted that, when present in a composite filling material, the polyunsaturated phosphate may also serve to promote adhesion between the inert filler and the binder, whereby to increase the strength of the cured material.



In order to further improve this property the polyunsaturated phosphate may be coated onto the inert filler before compounding it with the remainder of the ingredients of the composite filling material.

5 It should be noted that when the initiator system contains an amine the polyunsaturated phosphate may react or interfere therewith, thereby reducing the effectiveness of the initiator system. Accordingly, it is generally preferred that the initiator system does not contain an amine. However, this is not the case when the polyunsaturated phosphate is first applied to tooth material to act as an adhesion  
10 promoter as discussed above.

As will be appreciated, and in common with conventional composite filling materials, it is generally desirable that the catalyst or initiator be brought into contact with the polymerizable ingredient of the filling material only immediately before introduction of the  
15 filling material into a dental cavity. To this end, it is common practice to put up composite filling materials as two-part packs, one part containing the initiator and the other part containing the accelerator, the inert filler and polymerisable components being mixed with either or both of these two constituents. Where, however,  
20 the materials are intended to be polymerized by light or ultraviolet radiation, the material may be put up as a single pack.

The adhesion promoting compositions of the invention may also be used to improve the adhesion to tooth enamel, of orthodontic appliances when using as adhesives a composite material or a polymerizable composition comprising one or more unsaturated materials such as are used as  
5 binders in composite filling materials.

Thus, for example, the polyunsaturated phosphate may be used as an adhesion promoter for the treatment of enamel to which orthodontic brackets or bands are to be attached or, in periodontics, for the treatment of enamel to which a splint is to be attached. Further,  
10 they may be used as adhesion promoters in the build up of teeth with composite materials and the attachment of acrylic veneers via a composite or unfilled resin for the same purpose. Similarly they may be used as adhesion promoters in the attachment of single unit pontics to the abutment teeth via a composite or unfilled resin.

15 It has also been found that the adhesion promoters of the present invention may be used to promote the adhesion of composite materials as described above to metal substrates and in this connection can find application in the construction of crowns and bridges in which a polymeric material is bonded to the framework or substrate  
20 formed of a metal such as a chromium/cobalt alloy, a gold/copper alloy or the like.

The adhesion promoter of the invention may also be used to improve the adhesion of adhesive materials containing polymerizable ethylenically unsaturated material to substrates other than tooth material, for example metallic substrates formed of metals such as chromium/cobalt alloys, gold/copper alloys or the like.

In order that the invention may be well understood the following examples are given by way of illustration only.

EXAMPLE 1

Pentaerythritol triacrylate phosphate (PETAP)

A solution of technical pentaerythritol triacrylate (15.2 g) and triethylamine (10.1 g) in dry ether (50 ml) was slowly added with stirring to a solution of phosphorus oxychloride (15.3 g) in dry ether, at 0°C. After stirring for two hours at room temperature the triethylamine hydrochloride formed was filtered off and the product remaining in solution hydrolysed by addition of the ether solution to water (50 ml) with stirring. The resultant mixture was separated and the separated ether layer was then extracted with sodium carbonate solution. The extract was then acidified and the oily precipitate formed was extracted into ether. The ether extract was dried over magnesium sulphate and the ether was then removed from the dried extraction under reduced pressure to give the title compound as a clear colourless viscous oil, the infra-red absorption spectrum of which shows absorption peaks at 2800-2560; 1730; 1640; 1620; 1270; 1190 and 1060  $\text{cm}^{-1}$ .

EXAMPLES 2 AND 3

Following the procedure of Example 1, pentaerythritol trimethacrylate phosphate (PETMAP) and dipentaerythritol pentaacrylate phosphate (DPEPAP) were produced from pentaerythritol triacrylate and dipentaerythritol pentaacrylate, respectively. The two products had infra-red absorption spectra as shown in Table 1.

TABLE 1

| Product | Absorption peaks, $\text{cm}^{-1}$                      |
|---------|---|
| PETMAP  | 2600-2560; 1730; 1640; 1295; 1160;<br>1060; 1020.       |
| DPEPAP  | 2800-2560; 1730; 1640; 1620; 1300;<br>1270; 1190; 1060. |

A sample of the PETMAP was converted to its sodium salt (Na PETMAP) by reaction with sodium hydroxide.

Test 1

The effects of the above proposed compounds in improving the adhesion of dental material to teeth were tested as follows:

Extracted human teeth stored in 1% saline containing 1% formaldehyde, were ground on a flat glass slab with 600 grit Carborundum powder, to give a flat enamel (or dentine) surface about 4 mm in diameter. This was dried with compressed air and a 1% w/v solution of the polymerisable phosphate ester in absolute ethanol was applied with a fine brush or cotton wool wad; excess material and solvent were blown off with compressed air.

Composite material as described in the example of Patent Specification No. 1401805 was sandwiched between a freshly prepared cylinder formed from the composite (3mm diameter and approx. 15 mm long) and the prepared tooth surface, and held in place with a 200g weight. Excess composite was carefully removed and the composite allowed to harden at 37°C. After storage of the samples in water at 37°C for 24h, adhesion of the cylinders to the tooth substance was measured by pulling them apart in an Instron Universal Testing Machine at a cross-head speed of 0.01 cm/sec. The results for various treatments are given in Table 2.

By way of comparison the above procedure was repeated except that (i) no polymerizable phosphate was employed, (ii) no polymerizable phosphate was employed but the tooth enamel was first subjected to an acid etch, or (iii) a polymerizable phosphate containing only one ethylenically unsaturated group per molecule was employed (hydroxyethyl methacrylate phosphate HMAP). The results of these tests are also shown in Table 2.

TABLE 2  
Adhesion of Composite material to tooth substance

|    | <u>Treatment</u> | <u>Substrate</u> | <u>Average<br/>adhesion MPa</u> | <u>Number of<br/>Samples</u> |
|----|------------------|------------------|---------------------------------|------------------------------|
| 5  | PETAP            | Enamel           | 7.6                             | 8                            |
|    | PETMAP           | Enamel           | 8.8                             | 7                            |
|    | PETMAP           | Dentine          | 2.4                             | 8                            |
|    | Na PETMAP        | Enamel           | 8.2                             | 8                            |
|    | DPEPAP           | Enamel           | 7.8                             | 8                            |
| 10 | None             | Enamel           | 0.19                            | 8                            |
|    | Acid Etch        | Enamel           | 8.1                             | 6                            |
|    | HMAP             | Enamel           | 2.7                             | 9                            |

15      Tooth enamel treated as above using a PETMAP-containing adhesion promoter showed an average adhesion of 7.6 MPa (for 8 samples), after storage in water at 37°C for three months.

### Test 2

Tests were also conducted to ascertain the degree of protection against micro leakage afforded by the use of the polymerisable phosphates.

15      Extracted human teeth were selected for the absence of caries and cracks, coated with nail varnish, and set into resin with the crown exposed. Two diametrically opposed cavities, approximately

3 mm in diameter and extending about 2 mm into the dentine, were prepared in each tooth using a high speed handpiece, then thoroughly cleaned and dried with a dental air/water syringe. A cotton wool wad was used to apply a 1% w/v solution of the polymerisable phosphate ester in absolute ethanol to one cavity tooth, and the solvent evaporated with compressed air.

Composite resin as described above was then placed in the cavity, held under pressure with a matrix strip while it hardened, and finally finished with a medium grit abrasive disc lubricated with "Vaseline". The second cavity in the tooth was similarly filled and finished, but without using the phosphate ester pretreatment.

After cycling the teeth for 24 hours between four water baths containing 0.1% acid fuchsin and held at 37° - 10° - 37° - 55°C, with an immersion time in each bath of approximately 2 seconds, the cavities were sectioned and leakage of dye between the composite and tooth substance assessed. For twenty-three teeth, sixteen untreated cavities showed more leakage than their treated counterpart, while only three treated cavities showed greater leakage than their untreated counterpart. Statistical analysis shows that the use of the polymerisable phosphate ester as pretreatment gives a highly significant reduction in marginal leakage.

### TEST 3

In order to evaluate the effectiveness of the polyunsaturated phosphates as coating materials for inert filler in composite materials,

a composite material was produced as disclosed in the example of Patent Specification No. 1401805 except that there was used as inert filler a synthetic hydroxy apatite having a particle size of less than 60 microns. A sample of the composite material was made up and the transverse tensile strength thereof was measured. When using an untreated hydroxy apatite, the transverse tensile strength was about 35 Mpa but when employing one which had been coated by slurring it with a 1% w/v solution of PETMAP in ethanol and then removing the ethanol under reduced pressure, the transverse tensile strength was about 70 Mpa.

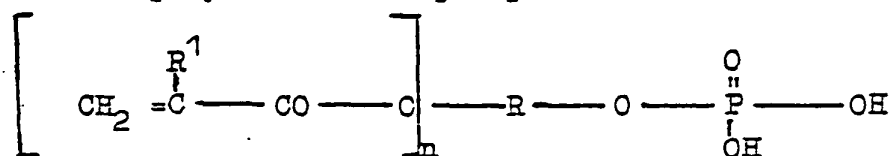


CLAIMS

1. An adhesion promoter composition, suitable for improving the adhesion of a composite dental filling material to natural teeth, characterised in that it comprises a solution in a volatile organic solvent there-  
5 for, of a polyethylenically unsaturated monophosphate or salt thereof, the unsaturated monophosphate contain-  
ing a monophosphate radical of the formula  $\text{-C-P}^{\text{O}}(\text{OH})_2$  and  
at least three ethylenically unsaturated groups per mol-  
ecule.
- 10 2. A composition as claimed in Claim 1, characterised in that the solvent is a lower aliphatic alcohol.
3. A composition as claimed in Claim 1 or Claim 2, characterised in that the solution contains from 0.5 to 10% by weight of polyunsaturated phosphate.
- 15 4. A composition as claimed in any one of the preceding claims characterised in that the ethylenically unsaturated groups in the polyunsaturated phosphate are terminal ethylenically unsaturated groups.
5. A composition as claimed in Claim 4, characterised  
20 in that the polyunsaturated phosphate is a monophosphate ester of a polyhydric alcohol containing at least four

hydroxyl groups in which at least three hydroxyl groups are esterified with an ethylenically unsaturated carboxylic acid.

- 5 6. A composition as claimed in Claim 5, characterised in that the polyunsaturated phosphate has the formula:



in which:

- 10 R is an aliphatic radical (which may be interrupted by one or more oxygen atoms), or a cycloaliphatic radical or aryl radical having a valency of  $n + 1$  and containing from 4 to 16 carbon atoms;

$\text{R}^1$  is a hydrogen or halogen atom or a cyano or  $\text{C}_1\text{-C}_3$  alkyl group; and

$\underline{n}$  is an integer of at least 3.

- 15 7. A composition as claimed in Claim 6, characterised in that the polyunsaturated phosphate is pentaerythritol triacrylate monophosphate, pentaerythritol trimethacrylate monophosphate, dipentaerythritol pentaacrylate monophosphate or dipentaerythritol pentamethacrylate mono-  
20 phosphate.

8. A method of dental treatment by polymerizing a dental material comprising a polyethylenically unsaturated material and an initiator therefor in contact with tooth material, characterised in that the tooth material  
5 is first treated with a polyethylenically unsaturated monophosphate or salt thereof containing a monophosphate group of the formula  $\text{-O}-\overset{\text{O}}{\underset{\text{||}}{\text{P}}}(\text{OH})_2$  and at least three ethylenically unsaturated groups per molecule.
9. A method as claimed in Claim 8, characterised in  
10 that the polyunsaturated monophosphate is as defined in any one of Claims 4-8.
10. A method as claimed in Claim 8 or Claim 9, characterised in that the dental material is a composite dental filling material containing ethylenically unsaturated  
15 material, initiator and an inert filler.
11. A dental filling material characterised in that it comprises a polymerizable ethylenically unsaturated material, an initiator therefor, inert filler and a polyethylenically unsaturated monophosphate or salt thereof  
20 containing a monophosphate radical of the formula  $\text{-O}-\overset{\text{O}}{\underset{\text{||}}{\text{P}}}(\text{OH})_2$  and at least three ethylenically unsaturated groups per molecule.

12. A filling material as claimed in Claim 11, characterised in that polyunsaturated phosphate is as defined in any one of Claims 4-8.

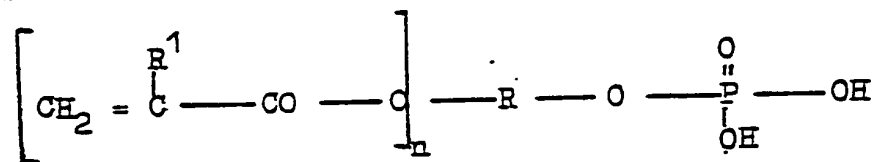
5 13. An adhesion promoter suitable for improving the adhesion of a free radical polymerizable resin to a substrate comprising a polyethylenically unsaturated monophosphate or salt thereof containing a monophosphate radical of the formula  $-O-\overset{\overset{O}{\parallel}}{P}-(OH)_2$  and at least three ethylenically unsaturated groups per molecule.

10 14. An adhesion promoter as claimed in Claim 13, characterised in that the polyunsaturated monophosphate is as defined in any of Claims 4-8.

15 15. A method of adhering a free radical addition polymerizable resin to a substrate characterised in that the substrate is first treated with a polyethylenically unsaturated monophosphate or salt thereof containing a monophosphate group of the formula  $-O-\overset{\overset{O}{\parallel}}{P}-(OH)_2$  and at least three ethylenically unsaturated groups per molecule.

20 16. A method as claimed in Claim 15, in which the polyunsaturated monophosphate is as defined in any of Claims 4-8.

17. Polyethylenically unsaturated monophosphates of the formula:



and salts thereof, in which:

5 R is an aliphatic radical (which may be interrupted by one or more oxygen atoms), a cycloaliphatic radical or an aryl radical having a valency of  $n + 1$  and containing from 4 to 16 carbon atoms,

10  $\text{R}^1$  is a hydrogen or halogen atom or a cyano of  $\text{C}_1\text{-C}_3$  alkyl group; and

$n$  is an integer of at least 3.

18. Compounds as claimed in Claim 17, characterised in that  $n$  is an integer of from 3 to 6.

19. Pentaerythritol triacrylate monophosphate.

15 20. Pentaerythritol trimethacrylate monophosphate.

21. Dipentaerythritol pentaacrylate monophosphate.

22. Dipentaerythritol pentamethacrylate monophosphate.

